CALCULATION OF THE FORCES ACTING ON AN IMPURITY OF A METAL SUBJECTED TO A TEMPERATURE GRADIENT

Maurice Gerl

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by

Maurice Gerl

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CALCULATION OF THE FORCES ACTING ON AN IMPURITY OF A METAL SUBJECTED TO A TEMPERATURE GRADIENT

ABSTRACT—Within the limits of the stated approximations it is shown that in the case of self-diffusion the friction of charge carriers contributes little to the heat transport of the point defect, at least in normal metals. In transition metals the contribution of the electrostatic force due to the thermoelectric field may be much greater (approximately 0.1 eV in Pt).
It is shown that in thermal diffusion of impurities the effect of carrier friction can be substantial for elements whose valences differ from that of the matrix.
The evaluation of the phonon contribution is described as inconclusive due to the lack of data on phonon scattering by impurities.

The thermodynamics of irreversible processes permits a formal calculation of the flow of the impurities of a metal when the latter is placed in a temperature gradient. It expresses this flow as a function of the generalized forces of the system by means of phenomenological coefficients which are functions of the heats of transport of the impurities and of the atoms of the matrix [1]. / 1*

The microscopic meaning of the heat of transport is a much debated question, particularly when the impurities studied are vacancies of the metal (self-diffusion). Several authors relate the heat of transport of the vacancies of a metal to the characteristic parameters of self-diffusion (energy of formation and migration of vacancies) by phenomenological methods. They generally assume that the diffusing species receives a certain amount of energy at a given temperature from the metal lattice and gives it up to the lattice at a different temperature [2, 3, 4]. The weakness of these calculations lies in the difficulty of assigning a well-defined temperature to localized zones of the lattice during the diffusion process. A more elaborate calculation of the Brownian movement of the diffusing particle [5] relates the heat of transport to the migration energy of the metal atoms.

In any event, the thermal diffusion of impurities in a metal results from forces of two types:

(a) A force of chemical origin arising from the chemical potential gradient of the impurity in the temperature gradient, and

(b) A force of interaction between the heat-carrying agents (phonons, electrons of positive holes) and the impurities. This contribution q* to the heat of transfer should therefore be expressed as a function of the electrical and thermal characteristics of the matrix metal and of the impurity. The calculation given here, suggested by a paper given by Professor Huntington at Münster (Westphalia,

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*Numbers in the margin indicate pagination in the foreign text.

Germany, 1965) constitutes an attempt in this direction. For reasons of convenience, this contribution will be broken down into two terms:

$$q^* = q_e^* + q_p^*$$

q_e^* expressing the interactions between an impurity and electrons or an impurity and positive holes, and q_p^* expressing the interactions between phonons and an impurity.

In Section I, the calculation of q_e^* is carried out by means of two different methods, but by using the same type of approximation. The first, similar to the semiclassical calculation of interactions between electrons and impurities of a metal placed in an electric field [6], enables one to give an order of magnitude of q_e^* for the diffusion of interstitials, but it is difficult to apply to the case of /2 substitutionals and self-diffusion. The second method, derived from the calculation of Bosvieux and Friedel [7] for the same type of interactions, permits an estimation of q_e^* for self-diffusion and the diffusion of substitutionals.

Section II concerns the determination of the forces of interaction between phonons and impurities. The Debye model, also used by Schottky [18], permits an approximate calculation of q_p^*. The validity of this model is debatable at the temperatures customarily used in diffusion experiments.

In Section III, the contribution q_p^* of electron-impurity interactions to the heat of transfer is calculated for several impurities in Cu, Ag and Au. The contribution q_p^* of the phonon-impurity interactions is given as an example for self-diffusion in Cu.

SECTION I /3

CALCULATION OF THE FORCE $\underset{\sim}{F}e$ OF ELECTRIC ORIGIN

1 - Approximations Used

Figure 1 gives the notations used in the calculation.

The impurity placed at 0 diffuses the charge carriers characterized by their wave vector $\underset{\sim}{k}$, their density $n(\underset{\sim}{k})$ in the space of k's and their velocity $\underset{\sim}{v}(\underset{\sim}{k})$. The flow of carriers $\underset{\sim}{k}$ is therefore:

$$d\underset{\sim}{j}(\underset{\sim}{k}) = n(\underset{\sim}{k}).\ \underset{\sim}{v}(\underset{\sim}{k}).\ d_3 k \qquad (I.I.1)$$

The number of carriers diffused in the solid angle $d\Omega$ fixed by angle θ is, per second

$$dN = d\underset{\sim}{j}(\underset{\sim}{k}).\ \sigma(k,\theta).\ d\Omega \qquad (I.I.2)$$

$\sigma(k, \theta)$ being the differential effective diffusion cross section.

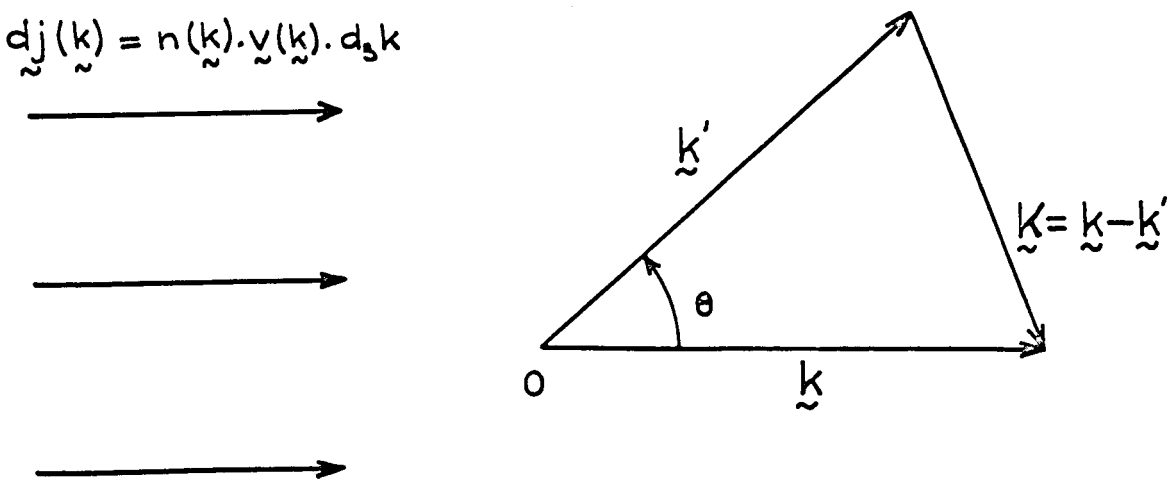


Figure 1.

The adiabatic approximation, which assumes that the impurity remains /4
stationary in the course of the diffusion $\underset{\sim}{k} \rightarrow \underset{\sim}{k}$'s is justified by the fact that the vibration frequencies of the atoms of a metal are of the order of 10^{12} sec $^{-1}$, whereas the time necessary for carriers of neighboring energy of the Fermi level to jump from a lattice site is of the order of 10^{-16} sec.

The elastic approximation assumes that in a $\underset{\sim}{k} \rightarrow \underset{\sim}{k}'$ transition, the momentum of the carrier remains unchanged, i.e., that the shock absorbs no energy:

$$|\underset{\sim}{k}| = |\underset{\sim}{k}'|$$

The momentum transferred to the impurity during the shock is therefore*:

$$\underset{\sim}{p} = \underset{\sim}{k} - \underset{\sim}{k'} = \underset{\sim}{K} \qquad \text{(I.I.3)}$$

2 - Semiclassical Calculation of $\underset{\sim}{F}e$

The momentum transfer per second from the carriers $\underset{\sim}{k}$ to the impurity is, in conformity with (I.I.1, 2 and 3):

$$\underset{\sim}{F}(\underset{\sim}{k}) = \int \underset{\sim}{K}.\, dN = \int \underset{\sim}{K}.\, n(\underset{\sim}{k}).\, v(\underset{\sim}{k}).\, \sigma(k,\theta).\, d\Omega.\, d_3k$$

or

$$\underset{\sim}{F}(\underset{\sim}{k}) = \underset{\sim}{k}.\, n(\underset{\sim}{k}).\, v(\underset{\sim}{k}).\, A(k).\, d_3k \qquad \text{(I.II.1)}$$

where A (k) is the effective resistivity cross section of electrons $\underset{\sim}{k}$:

$$A(k) = 2\pi \int_0^{\pi} \sigma(k,\theta).\, (1 - \cos\theta).\, \sin\theta.\, d\theta \qquad \text{(I.II.2)}$$

The total force acting on the impurity is therefore

$$\underset{\sim}{F} = \int \underset{\sim}{k}.\, n(\underset{\sim}{k}).\, v(\underset{\sim}{k}).\, A(k).\, d_3k \qquad \text{(I.II.3)}$$

with $\underset{\sim}{n}(\underset{\sim}{k}) = \frac{1}{4\pi^3}.\, \underset{\sim}{f}(\underset{\sim}{k})$ where f ($\underset{\sim}{k}$) is the distribution function of the electrons. We then have

$$\boxed{\underset{\sim}{F} = \frac{1}{4\pi^3} \int \underset{\sim}{k}.\, \underset{\sim}{f}(\underset{\sim}{k}).\, v(\underset{\sim}{k}).\, A(k).\, d_3k} \qquad \text{(I.II.4)}$$

2.1 Determination of the Distribution f ($\underset{\sim}{k}$) /5

The Boltzmann equation for the transport of carriers is written as

$$\frac{\partial f}{\partial t} + \underset{\sim}{v}.\, \underset{\sim}{\nabla}_r f + \frac{d\underset{\sim}{k}}{dt}.\, \underset{\sim}{\nabla}_k f + \left(\frac{\partial f}{\partial t}\right)_{coll} = 0 \qquad \text{(I.II.5)}$$

The distribution f ($\underset{\sim}{k}$, $\underset{\sim}{r}$, t) being little different from the distribution f_o ($\underset{\sim}{k}$, $\underset{\sim}{r}$, t) in the absence of perturbation, equation (I.II.5) can be linearized in the following manner, knowing that $f_o(E) = \left[1 + \exp\left(\frac{E - E_F}{kT}\right)\right]^{-1}$:

*The atomic units $|e| = \hbar = m = 1$ are subsequently used.

$$\underset{\sim}{\nabla}_r f \simeq \underset{\sim}{\nabla}_r f_o = -\frac{1}{T} \cdot \frac{\partial f_o}{\partial E} \cdot \left[E + T^2 \cdot \frac{d}{dT}\left(\frac{E_F}{T}\right) \right] \cdot \underset{\sim}{\nabla} T$$

$$\underset{\sim}{\nabla}_k f \simeq \underset{\sim}{\nabla}_k f_o = \frac{\partial f_o}{\partial E} \cdot \underset{\sim}{\nabla}_k E = \underset{\sim}{v} \cdot \frac{\partial f_o}{\partial E}$$

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \frac{f(\underset{\sim}{k}) - f_o(\underset{\sim}{k})}{\tau(\underset{\sim}{k})} = \frac{g(\underset{\sim}{k})}{\tau(\underset{\sim}{k})}$$

where $g(\underset{\sim}{k})$ is the deviation of the distribution from equilibrium,
$\tau(\underset{\sim}{k})$ is the relaxation time of electrons k.

If on the other hand the perturbation of the system is independent of time,

$$\frac{\partial f}{\partial t} = 0$$

Moreover,

$$\frac{d(\underset{\sim}{k})}{dt} = e \underset{\sim}{\mathcal{E}}$$

where e is the sign of the carrier charge and $\underset{\sim}{\epsilon}$ is the thermoelectric field.

The linearlized Boltzmann equation is then wirtten as

$$g(\underset{\sim}{k}) = \tau(\underset{\sim}{k}) \cdot \underset{\sim}{v}(\underset{\sim}{k}) \cdot \frac{\partial f_o}{\partial E} \cdot \left[-e\underset{\sim}{\mathcal{E}} + (E + T^2 \cdot \frac{d}{dT}\left(\frac{E_F}{T}\right)) \cdot \frac{\underset{\sim}{\nabla} T}{T} \right] \qquad (I.II.6)$$

From the expression of $g(\underset{\sim}{k})$ one can then calculate the force $\underset{\sim}{F}$, the energy flux $\underset{\sim}{W}_e$ and the thermoelectric field $\underset{\sim}{\epsilon}$ starting from the equation $\underset{\sim}{J} = 0$:

$$\underset{\sim}{F} = \frac{1}{4\pi^3} \int \underset{\sim}{k} \cdot v(\underset{\sim}{k}) \cdot g(\underset{\sim}{k}) \cdot A(k) \cdot d_3 k \qquad (I.II.7)$$

$$\underset{\sim}{J} = \frac{e}{4\pi^3} \int \underset{\sim}{v}(\underset{\sim}{k}) \cdot g(\underset{\sim}{k}) \cdot a_3 k = 0 \qquad (I.II.8)$$

$$\underset{\sim}{W}_e = \frac{1}{4\pi^3} \int \underset{\sim}{v}(\underset{\sim}{k}) \cdot \left[E(\underset{\sim}{k}) - E_F \right] g(\underset{\sim}{k}) \cdot d_3 k \qquad (I.II.9)$$

2.2 Calculation of $\underset{\sim}{\epsilon}$ and $\underset{\sim}{W}_e$ /6

By setting $u = T^2 \cdot \frac{d}{dT}\left(\frac{E_F}{T}\right)$ component J of $\underset{\sim}{J}$ in the direction of the temperature gradient and of the field $\underset{\sim}{\epsilon}$ can be written as

$$J = \frac{e}{4\pi^3} \int k \cdot \tau(\underset{\sim}{k}) \cdot k \cdot \frac{\partial f_o}{\partial E} \cdot \left[-e\mathcal{E} + (E + u) \cdot \frac{\nabla T}{T} \right] \cos^2 \theta \cdot d_3 k$$

By multiplying and dividing by the number of conduction carriers

$$N = \frac{1}{4\pi^3} \int f_o(\underset{\sim}{k}) \cdot d_3 k$$

and by defining the mean value of any quantity A (E):

$$< \tau . A\ (E).\ E^n > = \frac{\int 2 \frac{\partial f_o}{\partial E} .\ E^{n+1} .\ A\ (E).\ \tau\ (\underset{\sim}{k}).\ \cos^2 \theta .\ d_3 k}{\int f_o\ (E).\ d_3\ k} \qquad \text{(I.II.10)}$$

we have

$$J = N\ e^2 < \tau >. \mathcal{E} - N\ e. \left[< \tau . E > + u < \tau > \right] . \frac{\nabla T}{T} = 0$$

which permits the calculation of ϵ:

$$\boxed{e \mathcal{E} = \frac{1}{< \tau >} . \left[< \tau . E > + u . < \tau > \right] . \frac{\nabla T}{T}} \qquad \text{(I.II.11)}$$

The heat flux W_e is calculated in the same manner:

$$W_e = \frac{1}{4 \pi^3} \int (E - E_F) .\ k .\ \frac{\partial f_o}{\partial E} .\ k .\ \tau\ (\underset{\sim}{k}) . \left[- e \mathcal{E} + (E + u) . \frac{\nabla T}{T} \right] . \cos^2 \theta .\ d_3\ k$$

i.e., with the definition (I.II.10):

$$W_e = N\ e < \tau\ (E - E_F) > . \mathcal{E} - N . \frac{\nabla T}{T} . \left[< \tau\ E .\ (E - E_F) > + u < \tau\ (E - E_F) > \right]$$

Hence, with the value (I.II.11) of $e \epsilon$:

$$\boxed{W_e = - N . < \tau >. T . \nabla T \left[\frac{< \tau E^2 > < \tau > - < \tau E >^2}{T^2 < \tau >^2} \right]} \qquad \text{(I.II.12)}$$

The coefficient of electronic thermal conductivity K_e can therefore be written as

$$K_e = \mathcal{L} . T . \sigma$$

where $\sigma = N < \tau >$ is the electrical conductivity /7

$$\mathcal{L} = \frac{< \tau\ E^2 > . < \tau > - < \tau\ E >^2}{T^2 < \tau >^2}$$

is the Lorentz coefficient equal to $a\ \pi^2 k^2 / 3$ in the case of free electrons and of isotropic relaxation time.

2.3 Calculation of the Force $\underset{\sim}{F}$

In the same manner as for W and J, we obtain for the projection of F on the direction of $\underset{\sim}{\nabla T}$

$$F = \frac{1}{4\pi^3} \int k.\ k.\ \tau\ (\underset{\sim}{k}).\ \frac{\partial f_o}{\partial E}.\ k.\ A\ (k).\ \left[-\ e\mathcal{E} + (E+u)\ \frac{\nabla T}{T} \right].\ \cos^2 \theta.\ d_3\ k$$

or, with the value of ($e\epsilon$):

$$F = -\ (2)^{1/2}\ \left(\frac{m^*}{m}\right)^{1/2}.\ \sigma.\left[\frac{<\tau\ A\ E^{3/2}><\tau> - <\tau E><\tau A\ E^{1/2}>}{<\tau>^2} \right].\ \frac{\nabla T}{T} \qquad \text{(I.II.13)}$$

or

$$F = -\ (2)^{1/2}.\ m^{*1/2}.\ \frac{\sigma}{e^2}.\left[\frac{<\tau\ A\ E^{3/2}><\tau> - <\tau E><\tau\ A\ E^{1/2}>}{<\tau>^2} \right].\ \frac{\nabla T}{T}$$

in classical units.

We shall call $F_z(o)$ the force thus calculated, z being equal to the screening charge of the impurity whose effective resistivity cross section will be designated by $A_z(E)$. To simplify the calculation of the averages contained in the expression of $F_z(o)$ one can make the approximation of the isotropic relaxation time:

$$\tau\ (\underset{\sim}{k}) = \tau\ (E)$$

The bracket of equation (I.II.13) is then simply written as

$$C = \frac{\overline{\phi}_M \cdot \overline{\phi}_N - \overline{\phi}_0 \cdot \overline{\phi}_P}{(\overline{\phi}_Q)^2}$$

with

$$\overline{\phi} = \int_o^\infty \phi\ (E).\ \left(-\frac{\partial f_o}{\partial E}\right).\ dE = \phi\ (E_F) + \frac{1}{6}\ \pi^2\ (kT)^2.\left[\frac{\partial^2 \phi\ (E)}{\partial E^2} \right]_{E_F}$$

and /8

$$\phi_M\ (E) = E^{5/2}\ .\ A\ .\ \tau$$

$$\phi_N\ (E) = E\ .\ \tau$$

$$\phi_0\ (E) = E^2\ .\ \tau$$

$$\phi_P\ (E) = E^{3/2}\ .\ A\ .\ \tau$$

$$\phi_Q\ (E) = E.\ \tau$$

Neglecting the fourth-order terms in the calculation of C, we then simply have

$$C = \frac{1}{6}\pi^2 (kT)^2 \cdot A_z(E_F) \cdot E_F^{-1/2} \cdot \left[1 + 2 \left(\frac{dA/A}{dE/E}\right)_{E_F} \right] \quad \text{(I.II.14)}$$

This enables us to write the force $F_z(o)$ in the form

$$\frac{F_z(o)}{\nabla T} = -\frac{\sqrt{2}}{2} \cdot \left(\frac{\pi^2 k^2}{3}\right) \cdot T \cdot \sigma \cdot \left(\frac{m^*}{m}\right)^{1/2} \cdot E_F^{-1/2} \cdot A_z(E_F) \cdot \left[1 + 2 \left(\frac{dA/A}{dE/E}\right)_{E_F} \right]$$

or still more simply, since the coefficient of electronic thermal conductivity K_e is related to σ by the relation

$$K_e = \frac{\pi^2 k^2}{3} \cdot T \cdot \sigma$$

$$\frac{F_z(o)}{\nabla T} = -\frac{\sqrt{2}}{2} \cdot K_e \cdot \left(\frac{m^*}{m}\right)^{1/2} \cdot E_F^{-1/2} \cdot A_z(E_F) \cdot \left[1 + 2 \left(\frac{dA/A}{dE/E}\right)_{E_F} \right] \quad \text{(I.II.15)}$$

To obtain this equation, it was not necessary to make explicit use of the sign e of the electric charge carriers. Equation (I. II. 15) is therefore valid whether conduction takes place via electrons or via positive holes, within the limits of the approximations used for obtaining it.

Actually, this equation is easily interpreted by noting that the total flux J of the charge carriers is zero, but is in fact the sum of a flux J_c of "hot" carriers directed toward the cold regions of the system and a flux J_f of "cold" carriers directed in the direction of $\underset{\sim}{\nabla}T$:

$$J_c + J_f = J = 0$$

If the effective cross section of the impurity were independent of the energy of the carriers, the resultant force to which it would be subjected would be directed toward the cold regions, since the momentum brought by the hot carriers would be greater than that brought by cold carriers. This remark is contained in the coefficient 1 of the parenthesis of (I. II. 15).

The coefficient $\left(\frac{dA/A}{dE/E}\right)_{E_F}$ expresses the fact that the effective cross section for the diffusion of the carriers by the impurity varies with the energy. If this term is sufficiently negative, the effective cross section of the cold carriers is greater than that of the hot carriers, which can reverse the direction of the force relative to the preceding case.

The sign of the force on the impurity therefore results from the comparison of two processes: /9

(a) The momentum brought to the impurity by a hot carrier is greater than that brought by a cold carrier.

(b) The effective cross section of the hot carriers may be greater than that of the cold carriers, in which case the force $F_z(o)$ is obviously directed toward the cold regions.

If the effective cross section of the hot carriers is sufficiently lower than that of the cold carriers, $F_z(o)$ is directed toward the hot regions.

It is possible to predict the value of $(\frac{dA/A}{dE/E})_{E_F}$ theoretically if one neglects the size effect. It is certain, however, that the latter must play a major part in the process of diffusion of the carriers by the impurity. Therefore, in estimating $(\frac{dA/A}{dE/E})_{E_F}$ it is more correct to use the results of the thermoelectric power of impurities, when they exist [26].

On the other hand, the force $F_z(o)$ results from the diffusion of the conduction electrons by the localized potential of the impurity. This force can therefore express the thermal diffusion of interstitials, isolated point defects. On the other hand, a substitutional impurity diffuses by jumping into a vacancy in a nearest neighbor position. The diffusion potential of electrons is therefore the potential of two neighboring defects: vacancy and impurity.

In the case of self-diffusion, the diffusion potential is due to the juxtaposition of a vacancy and of a metal ion displaced from its equilibrium position. In the course of the jump of the ion into the vacancy, the electron configuration of the system varies up to the neck position where the impurity ion is located between "two half-vacancies." In order to have a complete knowledge of the force F in the course of the jump, it would thus be necessary to calculate the effective cross section $A(E_F)$ of the impurity ion at any point of its trajectory.

To our knowledge, this calculation has never been made. We shall therefore assume that neighboring point defects behave as if they were isolated and that their screening charge is independent of the presence of the neighboring defect. This approximation is certainly a very rough one, as shown by a recent calculation [8] of interactions between impurities in a metal.

In this approximation, one can calculate the force F resulting from the diffusion of electrons by the impurity, and the force Fl due to diffusion by the potential of the vacancy. This force Fl is obviously imparted to the ions in the vicinity of the vacancy, not to the vacancy itself. The force acting on the ion with jumps is therefore F + m Fl, where m is a certain coefficient of distribution which the force Fl over the neighbors of the vacancy.

In the semiclassical calculation presented in this section, one cannot calculate the coefficient m. Below, the force m Fl is identified with the force exerted on the impurity by the distortion of the screen of the neighboring vacancy, due to the external perturbation (thermoelectric field and temperature gradient).

3 - Calculation of $\underset{\sim}{F}$ in Quantum Mechanics [7]

In quantum mechanics, the force $\underset{\sim}{F}$ acting on the charge z' located at site b relative to the diffusion potential $V(\underset{\sim}{r})$ at the origin is

$$\underset{\sim}{F} = z' \int \frac{\underset{\sim}{r} - \underset{\sim}{b}}{\left|\underset{\sim}{r} - \underset{\sim}{b}\right|^3} \cdot \delta\rho\,(\underset{\sim}{r}) \cdot d_3 r \qquad \text{(I. III. 1)}$$

where $\delta\rho(\underset{\sim}{r})$ is the variation of electron density due to the impurity and to the external perturbations. The potential $V(\underset{\sim}{r})$ is also decomposable in the first order in perturbation /10

$$V\,(\underset{\sim}{r}) = V_o\,(\underset{\sim}{r}) + V_1\,(\underset{\sim}{r}) \qquad \text{(I. III. 2)}$$

where $V_o(\underset{\sim}{r})$ is the perturbing potential in the absence of an electric field and temperature gradient, and $V_1(\underset{\sim}{r})$ is the potential due to the latter two perturbations.

$V(\underset{\sim}{r})$ and $\delta\rho(\underset{\sim}{r})$ are related by the Poisson equation:

$$\Delta\, V\,(\underset{\sim}{r}) = -\,4\,\pi.\,\delta\,\rho\,(\underset{\sim}{r}) + 4\,\pi\,z.\,\delta\,(\underset{\sim}{r}) \qquad \text{(I. III. 3)}$$

where z is the screening charge of the impurity.

3.1 Determination of $\delta\,\rho\,(\underset{\sim}{r})$

In the Born approximation, the wave functions diffused by the potential $V\,(\underset{\sim}{r})$ are written as

$$\Psi_k\,(\underset{\sim}{r}) = \exp\,(i\,\underset{\sim}{k}.\,\underset{\sim}{r}) + g_k\,(\underset{\sim}{r}) \qquad \text{(I. III. 4)}$$

The variation of electron density $\delta\rho_k\,(\underset{\sim}{r})$ is therefore in the first order of perturbation

$$\delta\,\rho_k\,(\underset{\sim}{r}) = \Psi_k^*\,(\underset{\sim}{r}) \cdot \Psi_k\,(\underset{\sim}{r}) - 1 = g_k\,(\underset{\sim}{r}).\, e^{-i\underset{\sim}{k}.\underset{\sim}{r}} + \text{C.C.}$$

The total variation of electron density is therefore

$$\delta\,\rho\,(\underset{\sim}{r}) = \sum_k \delta\,\rho_k\,(\underset{\sim}{r}) \cdot f\,(\underset{\sim}{k}) = \frac{2}{(2\,\pi)^3} \int \delta\,\rho_k\,(\underset{\sim}{r}).\, f\,(\underset{\sim}{k}) \cdot d_3\,k$$

. f (k) being the distribution function of electrons

and $g_k\,(\underset{\sim}{r}) = -\,\frac{2}{(2\,\pi)^3} \cdot \int \frac{\exp i\underset{\sim}{k}'.\,(\underset{\sim}{r}-\underset{\sim}{r}')}{k'^2 - k^2 - i\,\eta} \cdot \exp\,(i\,\underset{\sim}{k}.\,\underset{\sim}{r}') \cdot V\,(\underset{\sim}{r}').\, d_3\,k'.d_3\,r'$

This makes it possible to write $\delta\rho\,(\underset{\sim}{r})$ in the form

$$\delta\,\rho\,(\underset{\sim}{r}) = -\,\frac{4}{(2\,\pi)^6} \cdot \int \frac{\exp i\,(\underset{\sim}{k}' - \underset{\sim}{k}).\,(\underset{\sim}{r} - \underset{\sim}{r}')}{k'^2 - k^2 - i\,\eta} \cdot V\,(\underset{\sim}{r}') \cdot f\,(\underset{\sim}{k}) \cdot d_3 k \cdot d_3 k' \cdot d_3 r' + \text{C.C.} \qquad \text{(I. III. 5)}$$

η being infinitely small and positive.

In the approximation where E_F is independent of temperature, formula (I, II, 6) makes it possible to write

$$\underset{\sim}{f}(\underset{\sim}{k}) = f_o(\underset{\sim}{k}) + \tau(\underset{\sim}{k}) \cdot \underset{\sim}{k} \cdot \frac{\partial f_o}{\partial E} \left[-e\underset{\sim}{\xi} + \frac{1}{2}(k^2 - k_F^2) \cdot \frac{\nabla T}{T} \right]$$

or by setting

$$\begin{cases} \underset{\sim}{a}_o(\underset{\sim}{k}) = -e \cdot \tau(\underset{\sim}{k}) \cdot \underset{\sim}{\xi} & \text{(I.III.6)} \\ \underset{\sim}{a}_2(\underset{\sim}{k}) = \frac{1}{2} \cdot \tau(\underset{\sim}{k}) \cdot \frac{\nabla T}{T} & \text{(I.III.7)} \end{cases}$$

$$\underset{\sim}{f}(\underset{\sim}{k}) = f_o(\underset{\sim}{k}) + \underset{\sim}{k} \cdot \frac{\partial f_o}{\partial E} \left[\underset{\sim}{a}_o(\underset{\sim}{k}) + \underset{\sim}{a}_2(\underset{\sim}{k}) \cdot (k^2 - k_F^2) \right] \qquad \underline{/11}$$

Setting $\underset{\sim}{K} = \underset{\sim}{k}' - \underset{\sim}{k}$ in the internal,

$\underset{\sim}{K} = \underset{\sim}{k} - \underset{\sim}{k}'$ in the conjugated complex integral (formula I.III.5), we have

$$\delta\rho(\underset{\sim}{r}) = -\frac{4}{(2\pi)^3} \cdot \int \exp(i\underset{\sim}{K} \cdot \underset{\sim}{r}) \cdot V(\underset{\sim}{K}) \cdot f(\underset{\sim}{K}) \cdot d_3 K \qquad \text{(I.III.8)}$$

where

$V(\underset{\sim}{K}) = \frac{1}{(2\pi)^3} \cdot \int V(\underset{\sim}{r}') e^{-i\underset{\sim}{K} \cdot \underset{\sim}{r}'} d_3 r'$ is the Fourier transform of $V(\underset{\sim}{r})$ and

$$\underset{\sim}{f}(\underset{\sim}{K}) = \int_{k=0}^{\infty} \underset{\sim}{f}(\underset{\sim}{k}) \cdot \left[\frac{1}{\underset{\sim}{K} \cdot (\underset{\sim}{K} + 2\underset{\sim}{k}) - i\eta} + \frac{1}{\underset{\sim}{K} \cdot (\underset{\sim}{K} - 2\underset{\sim}{k}) + i\eta} \right] \cdot d_3 k = f_o(\underset{\sim}{K}) + g(\underset{\sim}{K})$$

Let us calculate successively $f_o(\underset{\sim}{K})$ and $g(\underset{\sim}{K})$:

$$f_o(\underset{\sim}{K}) = \int f_o(\underset{\sim}{k}) \cdot \left\{ PP \frac{1}{\underset{\sim}{K} \cdot (\underset{\sim}{K} + 2\underset{\sim}{k})} + PP \frac{1}{\underset{\sim}{K} \cdot (\underset{\sim}{K} - 2\underset{\sim}{k})} + i\pi\delta \left[\underset{\sim}{K} \cdot (\underset{\sim}{K} + 2\underset{\sim}{k}) \right] - i\pi\delta \left[\underset{\sim}{K} \cdot (\underset{\sim}{K} - 2\underset{\sim}{k}) \right] \right\} \cdot d_3 k$$

i.e.,

$$f_o(\underset{\sim}{K}) = \pi k_F \cdot \left[1 + \frac{k_F}{K} \cdot \left(1 - \frac{K^2}{4k_F^2}\right) \cdot \mathrm{Log} \left| \frac{2k_F + K}{2k_F - K} \right| \right]$$

$$g(\underset{\sim}{K}) = \int_o^{\infty} \underset{\sim}{k} \cdot \frac{\partial f_o}{\partial E} \left[\underset{\sim}{a}_o(\underset{\sim}{k}) + \underset{\sim}{a}_2(\underset{\sim}{k}) \cdot (k^2 - k_F^2) \right] \cdot \left\{ PP \frac{1}{\underset{\sim}{K} \cdot (\underset{\sim}{K} + 2\underset{\sim}{k})} + PP \frac{1}{\underset{\sim}{K} \cdot (\underset{\sim}{K} - 2\underset{\sim}{k})} + i\pi\delta \left[\underset{\sim}{K} \cdot (\underset{\sim}{K} + 2\underset{\sim}{k}) \right] - i\pi\delta \left[\underset{\sim}{K} \cdot (\underset{\sim}{K} - 2\underset{\sim}{k}) \right] \right\} d_3 k$$

In the approximation of an isotropic relaxation time

$$\underset{\sim}{a}_o(\underset{\sim}{k}) = a_o(|\underset{\sim}{k}|)$$
$$\underset{\sim}{a}_2(\underset{\sim}{k}) = a_2(|\underset{\sim}{k}|)$$

We then have

$$\underset{\sim}{g}(K) = 2\,i\,\pi^2 \int_0^{\infty} k^3 \cdot \frac{\partial f_o}{\partial E} \cdot \left[a_o + a_2 (k^2 - k_F^2) \right] \cdot \cos\theta_K \, dk \cdot \int_0^{K} \left\{ \delta \left[K^2 + 2k K \cos\theta \right] - \delta \left[K^2 - 2k K \cos\theta \right] \right\} \cdot \cos\theta \cdot \sin\theta \cdot d\theta$$

for by integrating with respect to θ

$$\underset{\sim}{g}(K) = i\,\pi^2 \cdot \cos\theta_K \cdot \int_{K^2/8}^{\infty} \frac{\partial f_o}{\partial E} \left[-e\mathcal{E} + (E - E_F) \cdot \frac{\nabla T}{T} \right] \cdot \tau(E) \cdot dE$$

We then obtain the electron density of the system by replacing $\underset{\sim}{f}(K) = f_o(K) + \underset{\sim}{g}(K)$ by its expression in equation (I. III. 8)

$$\delta\rho(\underset{\sim}{r}) = \int \exp(i \underset{\sim}{K} \cdot \underset{\sim}{r}) \cdot V(\underset{\sim}{K}) \cdot \left[-\frac{k_F}{2\pi^2} \cdot g_o(\underset{\sim}{K}) - \frac{i \cos\theta \, K}{2\pi} \cdot a(\underset{\sim}{K}) \right] \cdot d_3 K \qquad \text{(I. III. 9)}$$

where it was assumed that /12

$$g_o(K) = 1 + \frac{k_F}{K} \left(1 - \frac{K^2}{4 k_F^2}\right) \operatorname{Log} \left| \frac{2k_F + K}{2k_F - K} \right| \qquad \text{(I. III. 10)}$$

and

$$a(K) = \int_{K^2/8}^{\infty} - \frac{\partial f_o}{\partial E} \left[-e\mathcal{E} + (E - E_F) \cdot \frac{\nabla T}{T} \right] \cdot \tau(E) \cdot dE \qquad \text{(I. III. 11)}$$

The result differs from that obtained by Bosvieux and Friedel in the fact that a (K) is not simply equal to $a = -e\epsilon \cdot \tau$, but involves the use of averages of the relaxation time $\tau(E)$ on the derived distribution $\partial f_o / \partial E$.

Equations (I. III. 9) and (I. III. 3) thus enable one to make a self-consistent calculation of $\delta\rho$ ($\underset{\sim}{r}$) and V ($\underset{\sim}{r}$), and hence to calculate the force $\underset{\sim}{F}$ given by equation (I. III. 1).

3. 2 Determination of the Force Acting on the Impurity Due to the Deformation of Its Own Screen

According to the above authors, the force exerted by the screening charge z of the impurity on a charge z' at site b in the case of a metal subjected to an electric field alone is written as

$$F(b) = -\frac{4\,a\,.\,z\,.\,z'}{3\pi} \cdot \left[J_o(b) - 2\,J_2(b) \right] \qquad \text{(I. III. 12)}$$

where we set

$$J_{2p}(b) = \int_0^{2k_F} \frac{K^3 j_{2p}(K b)}{\left[K^2 + (2k_F/\pi).g_o(K) \right]^2} dK$$

j_{2p} being the spherical Bessel function of order 2_p.

In the case of an impurity of a metal placed in a temperature gradient, a is a function of K (eq. I.III.11), so that the force exerted on the ion by the deformation of its own screen is written as

$$F_z(o) = -\frac{4 z^2}{3\pi} \int_o^{\infty} \frac{K^3}{\left[K^2 + (2k_F/\pi) g_o(K) \right]^2} .a(K) dK \qquad (I.III.13)$$

a (K) being given by equation (I.III.11).

On the other hand, the effective resistivity cross section of electrons of wave vector k, calculated in the self-consistent Hartree approximation, is written as [7]:

$$A_z(k) = \frac{4\pi z^2}{k^4} . \int_o^{2k} \frac{K^3 dK}{\left[K^2 + (2k_F/\pi) g_o(K) \right]^2} \qquad (I.III.14)$$

Comparison of the last two equations permits the calculation of $F_z(o)$, given in Appendix I:

$$F_z(o) = -\frac{4}{3\pi^2} . \int_o^{\infty} E^2 . A(E) \left(-\frac{\partial f_o}{\partial E}\right) . \left[-e\mathcal{E} + \frac{\nabla T}{T} (E - E_F) \right] \tau(E) . dE$$

On the other hand, using relations (I.II.10) defining the averages on the distribution $\delta f_o/\delta E$: /13

$$\langle \tau . A . E^n \rangle = \frac{2^{3/2}}{3\pi^2 N} . \int_o^{\infty} \left(-\frac{\partial f_o}{\partial E} \right) . E^{n+3/2} . \tau(E) dE$$

and the value (I.II.11) of the thermoelectric field, we have for $F_z(o)$:

$$F_z(o) = -2^{1/2} N \langle \tau \rangle \left[\frac{\langle \tau A E^{3/2} \rangle \langle \tau \rangle - \langle \tau E \rangle \langle \tau A E^{1/2} \rangle}{T^2 \langle \tau \rangle^2} \right] T.\nabla T \qquad (I.III.15)$$

The force acting on the impurity ion, due to the deformation of its own screen, is thus identified with the force due to the diffusion of carriers by the potential of the impurity.

3.3 Determination of the Force Due to the Deformation of the Screen of the Vacancy

What is more interesting to deduce from this calculation is the force $F_{-Z}(b)$ exerted by the deformation of the screen of the vacancy on the impurity ion of charge Z'. When the latter is in a lattice position adjacent to the vacancy, its screening charge is

$$z = Z' - Z$$

so that the vacancy, of charge -Z, "sees" an impurity of charge +Z.

According to (I. III. 12), we then have

$$\boxed{F_{-Z}(b) = \frac{4 a Z^2}{3 \pi} \cdot \alpha = m \cdot F_Z(o)} \qquad \text{(I. III. 16)}$$

where we have set

$$\alpha = J_o(b) - 2 J_2(b)$$

$$m = \frac{-\alpha}{J_o(0)}$$

3.4 Electrostatic Force

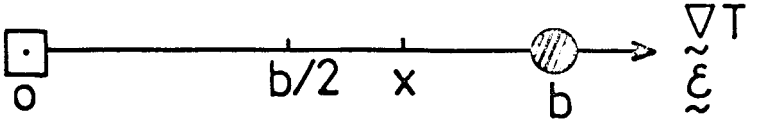
To the forces $F_z(o)$ and $F_{-Z}(b)$ is added the electrostatic force acting on the impurity ion. According to Bosvieux and Friedel, this force is, for the impurity in substitution:

$$\boxed{\underset{\sim}{F_S} = Z \underset{\sim}{\xi}} \qquad \text{(I. III. 17)}$$

where Z is the valence of the matrix containing the impurity (indeed, the latter screens itself until it has the same valence as the matrix).

When the impurity is in the neck position it is assumed to screen itself completely, like an interstitial, and hence is not subjected to any electrostatic force. /14

3.5 Determination of the effective force $\underset{\sim}{F_e}$ acting on an interstitial or substitutional impurity, or on an atom of the solvent near a vacancy. Figure 2 describes the situation.



Vacancy or interstitial site

Substitutional impurity or ion of the solvent or interstitial impurity

Figure 2.

Site b is the initial site of the diffusant species and site 0 is the final site; b/2 is the neck position. The following table can then be drawn up for the external forces acting on the diffusant species in the course of its displacement between b and b/2 (Table I).

The equivalent force for the net diffusion of these forces is obtained by joining the value of the force at the neck position to the value at the initial site via a sinusoid of period b.

Force F_e is thus calculated in the three cases most common in diffusion.

Section III gives an application of this force to the diffusion of impurities in Cu, Ag and Au.

Table 1. /15

Species	Position	Screening charge	Force on the ion
Interstitial impurity	b	Z'	$F_{Z'}(o)$
	b/2	Z'	$F_{Z'}(o)$
	Effective force Fe		$F_{Z'}(o)$
Substitutional impurity near a vacancy	b	Z' - Z	$Z\varepsilon + F_{-Z}(b) + F_{Z'-Z}(o)$
	b/2	Z'	$F_{Z'}(o)$
	x		$[Z\varepsilon + F_{-Z}(b) + F_{Z'-Z}(o)] + [F_{Z'}(o) - Z\varepsilon - F_{-Z}(b) - F_{Z'-Z}(o)] \cdot \sin^2(\frac{\pi x}{b})$
	Fe		$\frac{1}{2} \cdot [Z\varepsilon + F_{-Z}(b) + F_{Z'-Z}(o) + F_{Z'}(o)]$
Atom of solvent near a vacancy	b	0	$Z\varepsilon + F_{-Z}(b) = Z\varepsilon + m F_Z(o)$
	b/2	Z	$F_Z(o)$
	x		$[Z\varepsilon + m F_Z(o)] + [F_Z(o) - Z\varepsilon - mF_Z(o)] \cdot \sin^2(\frac{\pi x}{b})$
	Fe		$\frac{1}{2} \cdot [Z\varepsilon + (1+m) F_Z(o)]$

SECTION II

/17

CALCULATION OF THE FORCE $\underset{\sim}{F}_p$ DUE TO PHONONS

Exactly the same semiclassical calculation can be carried out for phonons as for electrons (paragraph II, Section I). The adiabatic and elastic approximations thus become much more debatable, since the group velocity $\underset{\sim}{v}_g$ of phonons tends to zero in the vicinity of the boundaries of the Brillouin zones. We shall use the Debye model, although it does not account for this decrease of $\underset{\sim}{v}_g$. On the other hand, the calculation is made in the first Brillouin zone, i.e., the Umklapp processes are neglected. This approximation is obviously very rough, since these processes are indispensable in accounting for the finite values of the thermal conductivity by phonons [9, p. 206].

I - Calculation of the Force $\underset{\sim}{F}_p$ and of the Heat Flux $\underset{\sim}{W}_p$

By analogy with (I.II.4), the force resulting from the diffusion of the phonons fixed by the wave vector $\underset{\sim}{q}$ is written as

$$\underset{\sim}{F}_p = \frac{\hbar}{8\pi^3} \cdot \int \underset{\sim}{q} \cdot f(\underset{\sim}{q}) \cdot v_g(\underset{\sim}{q}) \cdot A(q) \cdot d_3 q \qquad \text{(II.I.1)}$$

where $f(\underset{\sim}{q}) = f_o(\underset{\sim}{q}) + g(\underset{\sim}{q})$ is the distribution function of the phonons in the temperature gradient;

$A(q)$ is the effective cross section of thermal resistivity of the impurity:

$$A(q) = 2\pi \int_o^\pi \sigma(q,\theta) \cdot (1 - \cos\theta) \cdot \sin\theta \cdot d\theta \qquad \text{(II.I.2)}$$

We assume that only the longitudinal waves contribute to $\underset{\sim}{F}_p$. The linearized Boltzmann equation is then written as

$$\underset{\sim}{v} \cdot \underset{\sim}{\nabla}_r f_o + \frac{g(\underset{\sim}{q})}{\tau(\underset{\sim}{q})} = 0 \qquad \text{(II.I.3)}$$

with

$$f_o(\underset{\sim}{q}) = \frac{1}{\exp\left[u(\underset{\sim}{q})\right] - 1}, \text{ where } u(\underset{\sim}{q}) = \frac{\hbar\omega(\underset{\sim}{q})}{kT}$$

and

$$\underset{\sim}{v}(\underset{\sim}{q}) = \frac{\partial\omega}{\partial q} \cdot \frac{\underset{\sim}{q}}{q} = \frac{kT}{\hbar} \cdot \frac{\partial u}{\partial q} \cdot \frac{\underset{\sim}{q}}{q}$$

We then obtain for the deviation of the distribution function

$$g(\underset{\sim}{q}) = \frac{kT}{\hbar} \cdot \frac{\partial f_o}{\partial u} \cdot \frac{\partial u}{\partial q} \cdot u \cdot \tau(\underset{\sim}{q}) \cdot \frac{\underset{\sim}{q} \cdot \underset{\sim}{\nabla} T}{q \cdot T} \qquad \text{(II.I.4)}$$

In the approximation of isotropic relaxatiom time $\tau(q)$, the component $\underset{\sim}{F}_p$ /18 along $\underset{\sim}{\nabla} T$ is written as

$$F_p = \frac{\hbar}{6\pi^2} \cdot \left(\frac{kT}{\hbar}\right)^2 \cdot \frac{\nabla T}{T} \cdot \int_0^{q_M} \frac{\partial f_o}{\partial u} \cdot \left(\frac{\partial u}{\partial q}\right)^2 \cdot u \cdot \tau(q) \cdot A(q) \cdot q^3 \cdot dq \qquad \text{(II.I.5)}$$

Similarly, assuming that the spectrum of phonons of the three different polarizations is the same, the heat flux W_p can be written as

$$W_p = \frac{3\hbar}{6\pi^2} \cdot \left(\frac{kT}{\hbar}\right)^3 \cdot \frac{\nabla T}{T} \cdot \int_0^{q_M} \frac{\partial f_o}{\partial u} \cdot \left(\frac{\partial u}{\partial q}\right)^2 \cdot u^2 \cdot \tau(q) \cdot q^2 \, dq \qquad \text{(II.I.6)}$$

As can be readily verified, (II.I.6) is identical to the classical equation

$$W_p = -\nabla T \cdot \sum_{\text{polarizations}} \frac{1}{8\pi^3} \cdot \int_0^{q_M} C_v(q) \cdot v(q) \cdot \underset{\sim}{\Lambda}(q) \cdot d_3 q \qquad \text{(II.I.7)}$$

where we set $\underset{\sim}{\Lambda}(q) = v(q) \cdot \underset{\sim}{\tau}(q)$, $\underset{\sim}{\Lambda}(q)$ being the mean free path of phonons $\underset{\sim}{q}$.

$C_v(q)$ is the specific heat of phonons $\underset{\sim}{q}$ at constant volume.

Comparison of formulas (II.I.4) and (II.I.6) makes it possible to write

$$F_p = -\frac{1}{3} \cdot \left(\frac{\hbar}{kT}\right) \cdot K_p \cdot \nabla T \cdot \frac{\int_0^{q_M} \frac{\partial f_o}{\partial u} \cdot \left(\frac{\partial u}{\partial q}\right)^2 \cdot u \cdot \tau(q) \cdot A(q) \cdot q^3 \cdot dq}{\int_0^{q_M} \frac{\partial f_o}{\partial u} \cdot \left(\frac{\partial u}{\partial q}\right)^2 \cdot u^2 \cdot \tau(q) \cdot q^2 \cdot dq} \qquad \text{(II.I.8)}$$

A(q), the effective cross section of the defect whose diffusion is being studied, is difficult to calculate. Indeed, as in the case of electrons, a substitutional impurity must jump into a neighboring vacancy in order to diffuse. The defect which diffuses phonons is therefore a vacancy-impurity pair associated with the field of displacement of the atoms located in the vicinity of the pair. As a result, we can estimate the value of A (q) only very roughly. For the diffusion of phonons by point defects, A (q) is written as

$$A(q) = \beta q^4 \qquad \text{(II.I.9)}$$

where β is a coefficient taking into account the mass difference $\delta M/M$ of the impurity, the variation of the force constant $\delta f/f$ and the field of displacement $\delta R/R$ in the vicinity of the impurity [10]:

$$\beta = \frac{3a^6}{4\pi} \cdot \Delta^2 \qquad \text{(II.I.10)}$$

where

$$\Delta^2 = \frac{1}{12}\left(\frac{\delta M}{M}\right)^2 + \frac{1}{6}\left(\frac{\delta f}{f} - 12\frac{\delta R}{R}\right)^2$$

II - The Debye Model

In order to simplify equation (II.I.8), one can, for example, use the Deybe model:

$$\omega = S.\ q$$

where S is the velocity of sound in the solid, assumed isotropic and independent of q. /19

If in addition we set

$$\tau\ (q) = \frac{\Lambda}{S}$$

Λ being the mean free path of phonons, assumed independent of q, we have

$$F_p = -\frac{1}{3}\left(\frac{kT}{\hbar}\right)^4 . \frac{\beta}{S^5} . K_p . \nabla T . I \qquad \text{(II. II. 1)}$$

where

$$I = \frac{\int_0^{\Theta D/T} \frac{\partial f_o}{\partial u} . u^8 . du}{\int_0^{\Theta D/T} \frac{\partial f_o}{\partial u} . u^4 . du} \qquad \text{(II. II. 2)}$$

Θ_D being the Debye temperature.

III - Determination of the Effective Force $\underset{\sim}{F}_p$ acting on an interstitial impurity, substitutional impurity, or on an atom of solvent near a vacancy.

The situation is the same as that described in Figure 2. Unfortunately, for phonons the variation of the effective cross section A (q) with the position of the diffusant speicies is known even less than for electrons.

We shall therefore assume for diffusion by interstitials that the force is independent of the position of the diffusing atom. In the case of diffusion of an atom in substitution, coefficient β can be estimated when it is in an equilibrium position in the vicinity of a vacancy. On the other hand, when it is in a neck position, there is no information on A (q). We shall therefore assume, to have an order of magnitude for F_p, that the force of the phonon-impurity interaction remains constant along the path of the impurity.

This is obviously a very rough approximation.

SECTION III /21

FORCE ACTING ON A NOBLE METAL IMPURITY (Au, Ag, Cu)

Phenomenological equations show that in a temperature gradient, the entrainment velocity of a substitutional solute relative to the lattice is written in the form

$$v = -\frac{D}{kT}\left(kT\,\frac{\partial \text{Log } C}{\partial x} + \frac{\Delta E}{T}\,.\,\nabla T\right) \qquad \text{(III. 0. 1)}$$

$kT\,\frac{\partial \text{Log } C}{\partial x}$ represents the force of chemical origin due to the gradient of concentration C on the solute.

It can be shown that $\Delta E.\frac{\nabla T}{T} = \frac{Q^* - \Delta H_L}{T}\,.\,\nabla T$ is the force due to the fact that the system is subjected to a temperature gradient: ΔH_L is the enthalpy of formation of a vacancy in the vicinity of an atom of solute and Q* is the heat of transport of the solute.

The force of interaction between the heat-carrying agents and the metal solute should therefore be contained in the term ΔE. Whether this force participates in what is called Q* or whether it is added to Q* depends on the manner in which the phenomenological equations are written. Without trying to delve into this question any deeper, we shall write

$$\Delta E = \Delta E_1 + q^* \qquad \text{(III. 0. 2)}$$

q* being simply the contribution of the force due to electrons and phonons to the energy ΔE. Neglecting the electron-phonon interactions, one can then obviously separate the contribution of these two types of heat carriers.

$$q^* = -(Fe + Fp).\frac{T}{\nabla T} = q_e^* + q_p^* \qquad \text{(III. 0. 3)}$$

I - Determination of q^*_e for Different Solutes in Cu, Ag, Au

According to Table I, force F_e due to electrons is of the form

$$F_e = \frac{1}{2}\,Z\,\mathcal{E} + \frac{1}{2}\left[\,m\,F_{Z^{(o)}} + F_{Z'-Z^{(o)}} + F_{Z'^{(o)}}\,\right] \qquad \text{(III. 1. 1)}$$

Z is the valence of the matrix, Z' that of the solute, m is the coefficient of distribution on ions near a vacancy of the force due to the diffusion of electrons by the vacancy.

ϵ is the thermoelectric field in the system.

On the other hand, the forces $F_z(o)$ are given by equation (I. II. 15):

$$\frac{F_z(o)}{\nabla T} = - M. A_z (E_F). \left[1 + 2 E_F \alpha_1 \right] \text{ (ergs/deg)} \qquad \text{(III. I. 2)}$$

(a) $M = \left(\frac{m^*}{2 E_F}\right)^{1/2}$. K_e is a characteristic of the matrix.

For Cu, the thermal conductivity by phonons is sufficiently low so that K_e can be identified with the total thermal conductivity coefficient.

For Ag and Au, no experimental value of K_e exists at high temperature; in these metals, K_e was determined by the Wiedemann-Franz Law.

(b) $A_z(E_F)$ can be obtained experimentally by the resistivity measurements /22 on alloys of increasing concentration. Indeed, the impurity resistivity ρ_i of electrons of energy E is written as

$$\rho_i (E) = \frac{m^*}{n e^2 \tau} \qquad \text{(III. I. 3)}$$

with

$$\tau . A_z (E). v = \frac{1}{n_i}$$

where v is the velocity of electrons of energy E.

At a low concentration n_i of impurities, the concentration of conduction electrons n remains equal to n_o, the concentration in the pure metal, which makes it possible to write the total resistivity ρ_i in the form

$$\rho_i (E_F) = \frac{(2m^*)^{1/2} n_i}{e^2 n_o} . E_F^{1/2} . A_z (E_F) \qquad \text{(III. I. 4)}$$

In the univalent Cu, Ag, Au, n_i/n_o is equal to c_i, the atomic concentration of impurities, and the derivative of $\rho_i (E_F)$ at $c_i = o$ is written as [25]

$$\zeta_i = \frac{(2m^*)^{1/2}}{e^2} . E_F^{1/2} . A_z (E_F)$$

Or, if E_F is expressed in eV and $A_z(E_F)$ in $Å^2$:

$$\zeta_i = 0{,}211 . E_F^{1/2} . A_z (E_F) \; \mu\Omega.\text{cm/per cent} \qquad \text{(III. I. 5)}$$

$A_z(E_F)$ can thus be deduced from values of ζ_i published by Landolt and Börnstein and due to Lindc [27].

(c) $\alpha_1 = \left(\frac{dA}{A\,dE}\right)_{E_F}$ the derivative at the Fermi level of the effective resistivity cross section of the impurity, can be deduced from the variation at $c_i = o$ of the thermoelectric power S of alloys as a function of c_i. According to F. A. Otter [26], the derivative of S at the origin is given by the equation

$$\left(\frac{dS}{100\,dc_i}\right)_o = (\alpha_1 - \alpha_c).\ \frac{0{,}0243\ \zeta_i\ T}{\rho\ T} \qquad \text{(III. I. 6)}$$

where $\alpha_c = \frac{S_T}{T} \cdot \frac{1}{0{,}0243} - \frac{1}{2\ E_F}$ is the critical parameter α characteristic of the metallic matrix. S_T, ρ_T are the thermoelectric power and resistivity of the pure metal at the temperature of the measurement of S. /23

Let us note that this analysis is acceptable if the effective cross section A does not vary too rapidly in the vicinity of E_F ($|\alpha_1| \lesssim 0{,}2$).

The value of $\left(\frac{dS}{dC_i}\right)_{C_i = 0}$ thus permits the determination of α_1. For alloys of Cu, Ag and Au studied experimentally by Domenicali and Otter [25] and Otter [26], we used their values of α_1. For the other alloys, we resumed their analysis starting from measurements of the thermoelectric power given in the literature [28], [27]. The values of α_1 thus obtained are not always very reliable, since not many measurements of S on low concentration alloys have been made.

1. 1 Impurities in Cu at 1000°C

$E_F = 7$ eV, $m^* = m_e K_e = 3.15 \times 10^7$ erg/cm sec deg, so that the coefficient M is

$$M = 0.20\ \text{erg/cm}^2\ \text{deg}$$

Between 0 and 200°C, ρ_T is adequately represented by the equation

$$\rho_T = 6.10^{-3} T\ (\mu\Omega.\text{cm})$$

so that equation (III. I. 6) can be written in the form

$$\alpha_1 - \alpha_c = \frac{0{,}247}{\zeta_i} \cdot \left(\frac{dS}{100\,dC_i}\right)_o \quad (\text{eV})^{-1}$$

(a) Determination of the Forces $F_z(o)$

Table II summarizes the calculations made in order to obtain the force $F_z(o)$ acting on different impurities of screening charge $z = Z' - Z$ in copper.

The values α_1 marked with an asterisk are those obtained by Domenicali and Otter [25] and Otter [26]. In the case where no experimental value of the thermoelectric power exists, the same value of α_1 was taken within a given group of elements of Z. This is roughly justified by the fact that according to the theoretical value of $A_Z(E_F)$ (equation I. III. 14), α_1 is dependent on z alone. This identification obviously neglects the size effect.

(b) Calculation of the effective force F_e

According to Table I, the effective force F_e acting on an ion of solute is written as

$$\frac{F_e}{\nabla T} = \frac{1}{2} Z \left(\frac{e\mathcal{E}}{\nabla T}\right) + \frac{1}{2} \left[m \frac{F_Z(o)}{\nabla T} + \frac{F_{Z'-Z}(o)}{\nabla T} + \frac{F_{Z'}(o)}{\nabla T} \right]$$

For copper at 1000°C, $e\epsilon/\nabla T = 0.07 \times 10^{-4}$ eV/deg according to Landolt and Bornstein [27]. On the other hand, the calculation shows that m = 0.187.

The force $F_Z(o)$ exerted on a vacancy in copper has been identified with the force acting on an ion of Zn in the same matrix.

Table 2. FORCE $F_Z(o)$ ACTING ON AN IMPURITY OF SCREENING CHARGE z IN A Cu MATRIX /24

Solute	Z'	ζ_i $\mu\Omega.cm/at.\%$	$10^{16} A_z(E_F)$ cm^2	$(dS/dc)_o$ $\mu V/°C.at\ \%$	α_1 $(eV)^{-1}$	$10^4 F_z(o)/\nabla T$ (eV/deg)
Ag	1	0,14	0,25	- 0,094	+ 0,02	- 0,04
Au		0,55	0,98	- 0,12	+ 0,13	- 0,35
Zn	2	0,32	0,57	- 0,47	- 0,18	+ 0,11
Cd		0,30	0,54		(- 0,18)	+ 0,10
Hg		1	1,79		(- 0,18)	+ 0,34
Al	3	1,25	2,24	- 1,41	(- 0,06)	- 0,04
Ga		1,42	2,54		- 0,06 □	- 0,05
In		1,06	1,9		(- 0,06)	- 0,04
Si	4	3,95	7,07	- 5,5	- 0,22*	+ 1,84
Ge		3,79	6, 8		- 0,18 □	+ 1,3
Sn		2,88	5,15		- 0,22*	+ 1,34
P	5	6,7	12	- 8,67	(- 0,14)	+ 1,44
As		6,8	12,2		- 0,14 □	+ 1,47
Sb		5,4	9,7		(- 0,14)	+ 1,16
Pd		0,89	1,59		- 0,48*	+ 1,14
Pt		2,1	3,8		- 0,88*	+ 5,4
Mn		2,9	5,2		+ 0,20*	- 2,47
Ni		1,25	2,24		- 1,6 *	+ 6

□ Values deduced from measurements of Crisp and Henry [28].

The force $F_{Z'}(o)$ exerted on the solute in the neck position is identified with the force on an impurity in substitution of screening charge Z', and hence of valence Z' + Z = Z' + 1. In order to take the best possible account of the size effect, the impurities in substitution and in equivalent neck positions should follow each other in the periodic classification of the elements. For example, Cd in a neck position is assumed to be analogous to an In ion in substitution, whereas a Zn ion in a neck position behaves as Ga. This is certainly a very rough approximation, but it is unfortunately impossible to really know experimentally the effective resistivity cross section of a solute in the neck position.

In the case of the transition metals Pd, Pt, Mn and Ni, the force F acting on the ion was assumed to remain constant during the entire course of the jump, since the electronic structure of the impurity in the neck position is unknown.

Table III gives the result of calculations thus obtained (T = 1273°K).

From this table, the following considerations can be deduced:

The effective force acting on an ion of the matrix metal in the course of the jump is very weak, as well as for the ions of valence close to that of copper.

The force acting on an ion of solute can change sign during a jump, and this leads in particular to the low values obtained for Au, Zn, Cd and Hg. This shows that the value of the results given in Table III depends closely on the validity of the model which we employed to calculate the effective force. The lack of experimental results pertaining to the diffusion of impurities under a temperature gradient unfortunately does not permit us to verify the theory. /26

1.2 - Impurities in Ag at 900°C

E_F = 5.5 eV; $K_e = 3.6 \times 10^7$ erg/cm sec deg, which makes it possible to calculate the coefficient M:

$$M = 0{,}26 \text{ erg/cm}^2\text{.deg}$$

Between 0 and 200°C, $\rho_T = 5{,}95.10^{-3}\ T\ (\mu\Omega\text{.cm})$,

and

$$\alpha_1 - \alpha_c = \frac{0{,}245}{\zeta_i}\left(\frac{dS}{dc}\right)_o \qquad (eV)^{-1}$$

On the other hand, $(e\epsilon/\nabla T) = 9.10^{-6}$ (eV/deg) at 900°C, and m = 0.171.

Table IV summarizes the calculations made.

1.3 - Impurities in Au at 1000°C

Table 3. EFFECTIVE FORCE F_e ON DIFFERENT SOLUTES IN COPPER

Solute	Z'	Substitution $10^4 \frac{F_{Z'-Z}(0)}{\nabla T}$ (eV/deg)	Neck $10^4 \cdot \frac{F_{Z'}(0)}{\nabla T}$ (eV/deg)	Vacancy $10^4 \cdot \frac{m F_Z(0)}{\nabla T}$ (eV/deg)	$10^4 \cdot \frac{Fe}{\nabla T}$ (eV/deg)	$q_e = -\frac{F \cdot T}{\nabla T}$ (eV)	Direction of the force
ion Cu		0	+ 0,11 (Zn)	+ 0,02	+ 0,10	- 0,013	Force toward the hot side (C)
Ag	1	- 0,04	+ 0,10 (Cd)		+ 0,08	- 0,010	
Au		- 0,35	+ 0,34 (Hg)		+ 0,04	- 0,005	
Zn		+ 0,11	- 0,05 (Ga)	+ 0,02	+ 0,08	- 0,01	Force toward the hot side (C)
Cd	2	+ 0,10	- 0,04 (In)		+ 0,08	- 0,01	
Hg		+ 0,34	- 0,04 (In)		+ 0,20	- 0,025	
Al		- 0,04	+ 1,84 (Si)	+ 0,02	+ 0,95	- 0,12	Force toward the hot side (C)
Ga	3	- 0,05	+ 1,30 (Ge)		+ 0,72	- 0,09	
In		- 0,04	+ 1,34 (Sn)		+ 0,70	- 0,09	
Si		+ 1,84	+ 1,44 (P)	+ 0,02	+ 1,69	- 0,22	Force toward the hot side (C)
Ge	4	+ 1,30	+ 1,47 (As)		+ 1,43	- 0,18	
Sn		+ 1,34	+ 1,16 (Sb)		+ 1,30	- 0,17	
P		+ 1,44	(+ 1,44)	+ 0,02	(+ 1,49)	(- 0,19)	Force toward the hot side (C)
As	5	+ 1,47	(+ 1,47)		(+ 1,52)	(- 0,19)	
Sb		+ 1,16	(+ 1,16)		(+ 1,21)	(- 0,15)	
Pd		+ 1,14			+ 1,2	- 0,15	C
Pt		+ 5,4			+ 5,4	- 0,69	C
Mn		- 2,47			- 2,4	+ 0,30	F
Ni		+ 6			+ 6	- 0,76	C

E_F = 5,5 eV ; K_e = 2,4.10^7 erg/cm sec deg, whence

$$M = 0,17 \text{ erg/cm}^2.\text{deg.}$$

Between 0 and 200°C, $\rho_T = 8,2.10^{-3}T$ ($\mu\Omega$.cm)

and

$$\alpha_1 - \alpha_c = \frac{0,34}{\zeta_i} \left(\frac{dS}{dc}\right)_o \text{ (eV)}^{-1}$$

On the other hand, $\left(\frac{e\epsilon}{\nabla T}\right) = 3,7.10^{-6}$ (eV/deg) and m = 0.171. Hence, Table V.

Few measurements of the thermoelectric power have been made in Au, so that the theory cannot be applied satisfactorily.

1.4 - Discussion

All the above numerical calculations utilize the experimental values of $A_z(E_F)$ and α_1. These two quantities could of course be deduced from the formula (I. III. 14). Although the agreement with the experimental values is adequate for impurities close to Cu, Ag or Au in the classification, it becomes poor as soon as z = Z' - Z exceeds 2 or 3. Indeed, the self-consistent Hartree method predicts a variation of $A_z(E_F)$ in z^2, correct with z is low, but which becomes poor as soon as z becomes large. The correct variation of $A_z(E_F)$ is found theoretically by using the concept of the virtual bound level, and in this case the value of $A_z(E_F)$ given by (I. III. 14) is obviously incorrect.

On the other hand, the above calculations show that the contribution of the deformation of the screen of the vacancy to the effective force is relatively slight. This is probably due to the fact that we used the approximation of independent screens. This is undoubtably a fairly rough approximation, since the screen radii are of the order of interatomic distances.

The correct manner of solving the problem would be to determine theoretically the deformation of the following screen of the system with three point defects (see Figure 2): /29

the impurity ion in position x,

absence of the metal ion in positions 0 and b.

This calculation would permit the determination of the force F acting on the impurity ion at any point of its trajectory.

II - Determination of q^*_p for a Metal Ion of the Matrix

According to formula (II. II. 1), the force F_p is written as

Table 4. EFFECTIVE FORCE F_e ON DIFFERENT SOLUTES IN SILVER

Solute	Z'	ζi $\mu\Omega.cm/at\%$	$10^{16} A_{Z'-Z}$ cm^2	$(dS/dc)_o$ $\mu V/°C.at\%$	α 1 $(eV)^{-1}$	$10^4 \frac{F_{Z'-Z}(0)}{VT}$ eV/deg	$10^4 \frac{F_{Z'}(0)}{VT}$ eV/deg	$10^4 . \frac{Fe}{VT}$ eV/deg	q_e^* (eV)
Ag ion		0				0	+ 0,04 (Cd)	+ 0,07	-0,008 (C)
Cu	1	0,077	0,156		(-0,28)	0,052	+ 0,07 (Zn)	+ 0,11	-0,013 (C)
Au		0,36	0,73	- 0,59	-0,28	0,25	+ 0,08 (Hg)	+ 0,21	-0,025 (C)
Zn □		0,64	1,29	- 0,64	-0,12	+ 0,067	+ 1,02 (Ga)	+ 0,6	-0,070 (
Cd	2	0,38	0,77	- 0,38	-0,12	+ 0,044	+ 0,76 (In)	+ 0,45	-0,053) C
Hg		0,79	1,6		(-0,12)	+ 0,081	+ 0,97 (Tl)	+ 0,57	-0,067 (
Al □		1,95	3,94		(-0,21)	+ 0,84	+ 2,74 (Ge)	+ 1,84	-0,22 (
Ga	3	2,36	4,76	- 3,3	-0,21	+ 1,02	+ 2,74 (Ge)	+ 1,93	-0,23) C
In		1,78	3,6		(-0,21)	+ 0,76	+ 2,18 (Sn)	+ 1,52	-0,18 (
Tl		2,27	4,58		(-0,21)	+ 0,97	+ 2,32 (Pb)	+ 1,69	-0,20)
Ge □		5,5	11,1		-0,23	+ 2,74	+ 4,90 (As)	+ 3,86	-0,45 (
Sn	4	4,36	8,8	- 8,2	(-0,23)	+ 2,18	+ 4,20 (Sb)	+ 3,24	-0,38) C
Pb		4,65	9,4		(-0,23)	+ 2,32	+ 4,20 (Bi)	+ 3,31	-0,39 (
As □		8,5	17,2		-0,25	+ 4,90	(+ 4,90)	(+ 4,9)	(-0,57) (
Sb	5	7,25	14,7	- 13,2	(-0,25)	+ 4,20	(+ 4,20)	(+ 4,2)	(-0,5)) C
Bi		7,3	14,8		(-0,25)	+ 4,20	(+ 4,20)	(+ 4,2)	(-0,5) (
Pd		0,44	0,89		-1,13 *	+ 1,6	(+ 1,6)	(+ 1,6)	(-0,19) (C)
Pt		1,60	3,23		-0,95 *	+ 4,9	(+ 4,9)	(+ 4,9)	(-0,58) (C)
Mn		1,60	3,23		+0,28 *	- 2,14	(- 2,14)	(- 2,1)	(+0,25) (F)

□ Values deduced from measurements of Crisp and Henry [28].

Table 5. EFFECTIVE FORCE F_e ON DIFFERENT SOLUTES IN GOLD

Solute	Z'	ζ_i $\mu\Omega.cm/at\%$	$10^{16} A_{Z'-Z}$ cm^2	$(dS/dc)_o$ $\mu V/°C.at\%$	α 1 $(eV)^{-1}$	$10^4 \frac{F_{Z'-Z}(0)}{\nabla T}$ eV/deg	$10^4 \frac{F_{Z'}(0)}{\nabla T}$ eV/deg	$10^4 . \frac{Fe}{\nabla T}$ eV/deg	q_e^* (eV)
Au ion		0				0	- 0,05 (Hg)	0	0
Cu	1	0,45	0,91	- 0,11	+ 0,02	- 0,12	- 0,14 (Zn)	- 0,11	+ 0,014 (F)
Ag		0,36	0,73	- 0,29	- 0,17	+ 0,07	- 0,08 (Cd)	0	0
Zn		0,95	1,92	- 0,37	- 0,03	- 0,14			
Cd	2	0,63	1,27	- 0,26	- 0,04	- 0,08			
Hg		0,44	0,89		(- 0,04)	- 0,05			
Pd		0,41	0,83		- 1,70 *	+ 1,56	(+ 1,56)	(+ 1,6)	- 0,2 (C)
Pt		1,01	2,04		- 1,75 *	+ 3,94	(+ 3,94)	(+ 4)	- 0,5 (C)
Mn		2,41	4,87		+ 0,10 *	- 1,1	(- 1,1)	(- 1,1)	+ 0,14 (F)

$$F_p = -\frac{1}{3}\left(\frac{kT}{\hbar}\right)^4 \cdot \frac{\beta}{S^5} \cdot K_p \cdot \nabla T \cdot I$$

or

$$\beta = \frac{a^6}{8\pi} \cdot \left[\frac{1}{2}\left(\frac{\delta M}{M}\right)^2 + \left(\frac{\delta f}{f} - 12\,\frac{\delta R}{R}\right)^2 \right]$$

The variation of the elastic constant $\delta f/f$ and the displacement $\delta R/R$ of nearby ions close to the impurity are known only when the impurity is a vacancy of the metal. In this case, for an ion of the metal close to a vacancy, the coefficient β is written as

$$\beta = \frac{a^6}{8\pi}\left(\frac{\delta f}{f} - 12\,\frac{\delta R}{R}\right)^2$$

In order to calculate $\delta f/f$, let us note that when an ion is close to a vacancy, it is displaced by the presence of the latter by an amount δR such that the force exerted by the vacancy is equal and opposite to the force exerted on the ion by the entire lattice.

According to Huntington [15], the interaction potential between two ions in copper can be written as

$$V = 0{,}053 \exp\left[-13{,}9\,\frac{\delta R}{R} \right]$$

whence the variation of the elastic constant in the vicinity of the vacancy is

$$\frac{\delta f}{f} = \exp\left[-13{,}9\,\frac{\delta R}{R} \right] - 1$$

The knowledge of $\delta R/R$ thus gives the knowledge of $\delta f/f$.

As far as the coefficient of thermal conductivity K_p by phonons is concerned, it is difficult to know it accurately in metals, since the electronic conductivity is much greater than the lattice conductivity. We shall use the experimental results obtained by doping the metals studied so as to eliminate the electronic conductivity [16].

The calculation of q_p^* for a copper ion in the vicinity of a vacancy is summarized in the following table:

The result which we have obtained for q_p^* is therefore much smaller than those obtained by Schottky [18], deduced from a calculation based on the Rice dynamic theory. On the other hand, the approximation which we made (elastic scattering of phonons by the defects, isotropy of the relaxation time, Debye model) do not permit a great deal of confidence in the numerical value of the results obtained. /30

Table 6. EFFECTIVE FORCE ON A Cu ION

T (°K)	Θ_D (°K)	K_p erg/cm. sec deg	S cm/sec	$\delta R/R$	$\delta f/f$	β	I	q^*_p eV
1 273	339 [14]	$2,4.10^5$ [16]	$2,5.10^5$ [12]	- 0,02 [17]	+ 0,3	$3,1.10^{-48}$	$2,15.10^{-3}$	+ 0,18 (toward cold side)

CONCLUSION

The above results show within the limits of the approximations made that in the case of self-diffusion, the friction force of the charge carriers on the point defect contributes little to the heat of transport of the latter, at least in normal metlas. In transition metals the contribution of the electrostatic force due to the thermoelectric field could be much greater (of the order of 0.1 eV in Pt).

In the case of the thermal diffusion of impurities, the friction force of the carriers can be fairly high for elements of valence differnt from the matrix.

The contribution of phonons is difficult to calculate because information on the processes of scattering of phonons by an impurity is lacking.

On the other hand, it is a bit uncertain to try to decide the validity of the theory, since few experimental results are available. For example, for self-diffusion, the numberical values are fairly rare, in view of the difficulty of detecting very weak flows of vacancies. In the case where flows have been observed [11, 19, 20, 21, 22], the order of magnitude of the heats of transport of the vacancies could be explained by our calculation. However, it should be noted that in several experimental studies, no thermal diffusion of vacancies could be demonstrated [23, 24, 11].

APPENDIX I

Calculation of the Force $F_z(o)$

Using equations (I. III. 11) and (I. III. 13), we have for $F_z(o)$:

$$F_z(o) = -\frac{4z^2}{3\pi} \int_0^{\infty} \frac{K^3}{\left[K^2 + (2k_F/\pi)\, g_0(K)\right]^2} \left[\int_{\frac{K}{2}}^{\infty} -\frac{\partial f_o}{\partial x} \cdot f(x) . \tau(x) . dx \right] dK \quad (A.1)$$

f (x) being defined by the equation

$$f(x) = -e\mathcal{E} + \frac{\nabla T}{T}\left(\frac{x^2}{2} - E_F\right) \quad (A.2)$$

The effective resistivity cross section of electrons of wave vector k/2 scattered by the impurity is written [V] as:

$$A\left(\frac{k}{2}\right) = \frac{64\pi z^2}{k^4} \cdot \int_0^{k} \frac{K^3\, dK}{\left[K^2 + (2k_F/\pi)\, g_0(K)\right]^2} \quad (A.3)$$

This makes it possible to express $F_z(o)$ in the form

$$F_z(o) = -\frac{1}{3\pi^2} \int_0^{\infty} \frac{d}{dy}\left(A(y) . y^4\right) . \left[\int_y^{\infty} -\frac{\partial f_o}{\partial x} . f(x) . \tau(x)\, dx \right] . dy \quad (A.4)$$

where y = K/2.

Integrating equation (A.4), by parts, we simply have

$$F_z(o) = \frac{4}{3\pi^2} \cdot \int_0^{\infty} A(E) . E^2 . \tau(E) . \left(\frac{\partial f_o}{\partial E}\right) . \left[-e\mathcal{E} + \frac{\nabla T}{T}(E - E_F) \right] . dE \quad (A.5)$$

In order to compare the result this obtained with the semiclassical result (I. II. 15), let us note that

$$\langle \tau(E) . A . E^n \rangle = -\frac{2^{3/2}}{3\pi^2 N} \cdot \int_0^{\infty} \frac{\partial f_o}{\partial E} . E^{n+3/2} . A(E) . \tau(E) . dE$$

On the other hand, according to equation (I. II. 11), the thermoelectric field ϵ verifies the relation

$$-e\mathcal{E} = \left(-\frac{\langle \tau E \rangle}{\langle \tau \rangle} + E_F\right) . \frac{\nabla T}{T}$$

Taking these two equations into account, we now have for the force $F_z(o)$ / 32

$$F_z(o) = -\sqrt{2}\, N \langle \tau \rangle \cdot \left[\frac{\langle \tau A E^{3/2} \rangle \langle \tau \rangle - \langle \tau E \rangle \langle \tau A E^{1/2} \rangle}{T^2 \cdot \langle \tau \rangle^2} \right] T \cdot \nabla T \quad (A.6)$$

This is exactly the same as equation (I. II. 15) in the case where the effective mass of the carriers is equal to that of the electron.

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